5-1-1939

Electrolytic Manganese

George T. Derana

Derana, G.T.

ELECTROLYTIC MANGANESE

by

GEORGE T. DERANA

Submitted to the Department of Chemistry
in Partial Fulfillment of the Requirements for
the Degree of Bachelor of Science
in
Metallurgical Engineering

Montana School of Mines
Butte, Montana

May, 1939

ELECTROLYTIC MANGANESE

By

GEORGE T. DERANA

A Thesis
Submitted to the Department of Chemistry in Partial
Fulfillment of the Requirements for the
Degree of Bachelor of Science
in
Metallurgical Engineering

Montana School of Mines
Butte, Montana

May, 1939

ELECTROLYTIC MANGANESE

TABLE OF CONTENTS

ELECTROLYTIC MANGANESE

INTRODUCTION

The production of metallic manganese by electrolysis is of potential value for the recovery of this strategic metal from domestic deposits. These deposits are largely unsuitable for the production of ferromanganese, but they are amenable to low-cost leaching processes. There has been considerable investigation in the electrodeposition of manganese from aqueous solutions, and recently, the U.S. Bureau of Mines[123] has done much successful work with it. Although at present there is little use for the pure metal, it offers a needed supply for the study of the all important manganese alloys.

The purpose of this thesis was to try to confirm some of the works of previous investigators, and to try to obtain the suitable conditions for the electrodepostion of manganese from aqueous sulphate solutions. Results show that this can be done. With further investigation to increase the current efficiency a continuous electrolytic system with leach solutions should be commercially feasible.

The primary difficulty encountered is the rapid deterioration of the electrolyte during electrolysis. A heavy brown precipitate of insoluble hydrated manganese dioxide ($MnO(OH)_2$) forms at the anode,

1. Shelton, Royer, & Towne, U.S. B of M., R.I. 3406, July, 1938.
2. Koster, Shelton, & Knickerbocker, U.S. B of M, R.I. 3322, Oct.1936
3. Shelton & Royer, Tr. Electrochem. Soc. Vol. 74, p.447, (1938).

and sometimes black manganese oxides form at the cathode and interfere with the metallic deposits. This fouling of the solutions maybe somewhat regulated by the addition of buffer salts, but it could not be entirely eliminated.

The work done has been entirely qualitative and no attempts have been made to measure quantitative factors such as amounts and thicknesses of deposits. Except for later work on leach solutions, all tests were made on chemically pure salts.

The apparatus consisted of electrolytic cells of pyrex beakers and rectangular glass jars, lead anodes and copper cathodes, ammeter, voltmeter, and slide-wire resistance. Direct current was obtained from storage batteries. The normal period of each electroltic test was about 30 minutes.

PRELIMINARY EXPERIMENTS

The preliminary experiments were mainly exploratory to get acquainted with the behavior of fundamental processes. The first series of tests were made on pure manganese solution without any additional agents at various current densities and concentrations. No metallic deposits would form. The fouling of the solution was very rapid and dense. Heavy deposits of manganese oxides would form at the anode and only a very thin layer of non-coherent oxides would form at the cathode.

Tests were then tried with addition of ammonium sulphate. An electrolyte as used by the U. S. Bureau of Mines[3](25 grams of manganese as $MnSO_4$ and 100 grams of $(NH_4)_2SO_4$ per liter) was tried with lead anode and copper cathode at room temperature. The results were not very satisfactory as shown in Table 1.

3. Shelton & Royer, Tr. Electrochem. Soc., Vol. 74, p. 447 (1938)

Table I.

CURRENT DENSITIES (Amperes per cm sq)	DEPOSITS
0.002 - 0.010	none
0.013	black and coherent
0.038	same as above
0.040	black and non-coherent
0.060	slightly metallic

The same solution was electrolized at various temperatures from 20° C to 100° C with no noticable improvements in deposition.

It was observed that by varying the electrode distance the rate of brown precipitation in the electrolyte was decreased with the increase of electrode distance. Most of the experiments were made at about 10 centimeters. A reasonable distance between the electrodes is necessary to prevent treeing and also because the manganese deposit at the cathode will dissolve readily in the sulphuric acid formed at the anode if they are too close together.

ANODE REACTIONS

The brown precipitate at the anode starts to form almost immediately upon electrolysis. According to Van Ardsdale and Maier[4] the manganous ions from the sulphate solution oxidize to the quadrivalent state. Hydolysis then takes place to form the hydrated manganese dioxide. The reactions are as follow;

$$Mn^{\bullet\bullet} - 2e = Mn^{\bullet\bullet\bullet\bullet}$$

$$Mn^{\bullet\bullet\bullet\bullet} + 3\,H_2O = MnO(OH)_2 + 4\,H^{\bullet}$$

4. Van Arsdale & Maier, Tr. Electrochem. Soc., Vol. 33, p.109 (1918)

In an acid solution the lowest valence changes to a still higher valence than the quadrivalent. As the reaction below indicates, the manganous ion changes to the permanganate.

$$Mn^{\cdot\cdot} - 5\,e = Mn^{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}$$

$$2\,HMnO_4 + 3\,Mn^{\cdot\cdot} + 7\,H_2O = 5\,MnO(OH)_2 + 4\,H^{\cdot}$$

At the beginning of each electrolysis in fresh acid solutions the permanganate ions will color the electrolyte pink and then changes to the brown precipitate. This indicates the formation of the hydrated manganese dioxide.

The black deposit on the anode was often quite coherent. When dried in air, some of the surface deposit powders and flakes off. Part of this deposition was more than likely the anhydrous manganese dioxide. Mellor[5] states that the anodic deposit may also have the other oxides, especially, the $MnO.MnO_2 = Mn_2O_3$ in acid solutions.

Bradt and Oaks[6] think that the large amounts of manganese oxides precipitation is due to the oxygen overvoltage exhibited by the lead anode.

Several of these lead anodes have disintegrated before the experimentation was finished.

CATHODE REACTIONS

A metallic manganese deposit usually formed immediately on the cathode at the start of electrolysis, but most deposits tended to oxidize readily. Although hydrogen was liberated at the cathode, the oxides formed there ~~is~~ are believed to be due to the hydrolizing effects of the solutions.

5. Mellor, Inorganic Chemistry, Vol. 12, p. 261
6. Bradt and Oaks, Tr. Eledtrochem. Soc., Vol. 71, p. 279 (1937)

Even with neutral solutions , hydrolysis in presence of air takes place. The reaction at the cathode, according to Van Arsdale[4], is as follows;

$$2\ Mn^{++} + 2\ H_2O + = Mn_2O_3 + 4\ MnO(OH)_2$$

USE OF DIAPHRAGM

Repeated tests with various concentrations of electrolytes failed to show an appreciable improvement in deposition. It was, therefore, concluded that the rapid changing or oxidation of the electrolytes must be overcome before satisfactory results were to be obtained. The solution to this problem has been worked out quite successfully by the U. S. Bureau of Mines[1,2,3] by the use of a diaphragm.

Therefore, the next series of tests were made with the use of a diaphragm. Several diaphragms were made and tried before the one made of water-bag duck was found to be the best. The solutions were made of the following compositions;

Catholyte: 24 grams / liter of $MnSO_4$
70 grams / liter of $(NH_4)_2SO_4$

Anolyte: 6 grams / liter of $MnSO_4$
25 cc of H_2SO_4

The results at various current densities are shown in Table II.

Table II.

CURRENT DENSITIES (Amperes per sq cm)	DEPOSITS
0.0025 - 0.0125	none
0.014	slightly metallic
0.026	dark, coherent, and metallic
0.031	metallic and coherent
0.033	black and non-coherent

Table II (continued)

CURRENT DENSITIES (Amperes per sq cm)	DEPOSITS
0.035	Black non-coherent
0.041	gray and powdery
0.047	very slight metallic
0.050 - 0.080	none

The same brown precipitate formed at the anode, but the catholyte solution in the diaphragm remained clear. Sulphuric acid forms in the anolyte and becomes more concentrated as the electrolysis continues.

In some of the tests a slightly metallic deposit would form at the very beginning, and then become covered with the black oxide powder. When this occurred, it was not possible to obtain a coherent metallic deposit. At times (especially at higher current densities) the cathode deposit would be powdery gray.

CONTINUOUS ELECTROLYTIC SYSTEM

The last series of tests were devoted to the most successful for the electrolytic deposition of manganese. This was by continuous electrolysis in a circulating system and use of the diaphragm. The cell was a rectangular glass jar (20 x 10 x 10 cm) with an overflow spout on one side. The same diaphragm was used. The anolyte solution filled the cell and the catholyte was fed through a hole drilled on the top of the wooden frame in the diaphragm and discharged into the anolte compartment through the side. The same concentrations of solutions as above were used except that the process was started by diluting the electrolyte in the diaphragm to 25 grams of $MnSO_4$ per liter.

The results at various current densities are shown in Table III.

Table III.

CURRENT DENSITIES (Amperes per sq cm)	DEPOSITS
0.016	black and non-coherent
0.028	partly good metallic
0.040	same as above
0.050	good coherent deposit
0.068	same as above
0.074	coherent but dull metallic

The best deposit was obtained at a current density from 0.050 to 0.068 amperes per sq cm. The Bureau of Mines[1] operated favorably at about 0.02 amperes per sq cm. Obviously, this is considerably lower than that above.

The solution entering the diaphragm was almost neutral (very slightly acidic); that overflowing from the catholyte into the anolyte was basic; and the anolyte was definitely acidic because sulphuric was added and was continually formed at the anode.

Reduction of the oxides formed on the cathode within the diaphragm was tried by bubbling hydrogen gas in the catholyte compartment but it was of no avail.

AMMONIUM SULPHATE

The actual function of $(NH_4)_2SO_4$ as an aid in the deposition of manganese from sulphate solutions is not clearly understood. S. M. Shelton[1,3] claims it reduces the ohmic resistance of the electrolyte. Fink and Kolodney[7] state that the salt prevents the

7. Colin G. Fink & M. Kolodney, Tr. Electrochem. Soc., Vol. 71, p. 279, (1937)

precipitation of $Mn(OH)_2$ which would reduce the hydroxyl ion concentration and make the catholyte acidic. However, results have shown that the addition of $(NH_4)_2SO_4$ improves the deposit of metallic manganese and reduces the rate of brown precipitation.

ELECTROLYSIS OF LEACH SOLUTIONS

Similar tests by continuous electrodeposition were made on leach solutions from the calcine of the Domestic Manganese and Development Co., at Butte, Montana.

Leaching was done in a mechanical agitator by adding a half a pound of calcine per liter of spent electrolyte, and an addition of about 20 cc of H_2SO_4 per liter. Agitation was carried on for two hours and then the pulp was filtered through a Buchner funnel filter. Enough calcine was used to consume the available acid. Therefore, the leach solution was neutral. George W. Nichols[9] reports a 95% recovery on leaching Butte ores.

Deposition of manganese took place in about the same range of current densities as for the pure salt electrolyte. However, the silvery gray color could not be obtained; most of the deposits were dull and dark. A simple test for iron (ferrocyanide) was made on the leach solution, but it did not show the presence of iron. Therefore, the difficulty in obtaining a good metallic deposit could not be attributed to this impurity. Addition of ammonium hydroxide to the leach solution form a heavy flocculation, slightly brown in color. This was believed to be manganic hydroxide.

9. George W. Nichols, Tr. Electrochem. Soc., Vol. 62, p. 392, (1932)

SUMMARY

1. Preliminary work on manganese sulphate solution alone gave unsatisfactory results, and most of them are nonreproducible.

2. Separation of electrolytes by use of a diaphragm is essential for the deposition of metallic manganese.

3. Addition of ammonium sulphate to the catholyte is important to obtain good deposits.

4. Continuous electrodeposition in a circulating system appeared to be the best process.

5. Good deposits were difficult to obtain from leach solutions.

6. Hydrated manganese dioxide forms at the anode, and metallic manganese is obtainable at the cathode.

7. The best metallic deposits formed at a current density of about 20 amperes per square foot.

CONCLUSIONS

Metallic manganese can be successfully electrodeposited from aqueous sulphate solutions. The most economical and commercially practical method would be the continuous electrolysis of leach solutions in a circulating system. Future investigations along this line would be warranted. In view of the fact that more than 90% of the manganese production is consumed as ferromanganese, the possibility of co-deposition of manganese with iron would be worthy of consideration. Of great importance for the future development of local deposits would be further investigations on the manganese recovery from rhodocrosite ores.

ACKNOWLEDGEMENT

The author gratefully acknowledges the splendid guidance and assistance received from Dr. Alfred E. Koenig, Professor of Chemistry at Montana School of Mines.

BIBLIOGRAPHY

1) Shelton, S. M., Royer, M. B., and Towne, A.P.
U. S. Bureau of Mines, Report of Investigations 3406,
Progress Report 23, Metallurgical Division, pp. 3-16, July, 1938

2) Koster, J., Shelton, S. M., and Knickerbocker, R. G.,
U. S. Bureau of Mines, Report of Investigations 3322,
Progress Report 13, Metallurgical Division, pp. 29 - 37 (1936)

3) Shelton, S. M., and Royer, M. B.,
"Effect of Solution Concentration in Electrodeposition of
Manganese", Transactions of the Electrochemical Society,
Vol. 74, pp. 447 - 459, (1938)

4) Van Arsdale, G. D., and Maier, C. G.,
"The Electrolytic Behavoir of Manganese in Sulphate Solutions",
Transactions of the Electrochemical Society,
Vol. 33, pp. 109 - 129, (1918)

5) J. W. Mellor, "Comprehensive Treatise on Inorganic and
Theoretical Chemistry", Vol. 12, (1932)

6) Bradt, W. E., and Oaks, H. H.
"The Electrodeposition of Manganese from Aqueous Solutions"
Part II, Sulphate Electrolytes, Transactions of the Electro-
chemical Society, Vol. 71, pp. 279 - 286, (1937)

7) Fink, Colin H., and Kolodney, M.,
Electrodeposition of Manganese Using Insoluble Anodes",
Transactions of the Electrochemical Society,
Vol. 71, pp. 287 - 300, (1937)

8) Oaks, H. H., and Bradt, W. E.,
"The Electrodeposition of Manganese from Aqueous Solutions", Part I, Chloride Electroltes, Transactions of the Electrochemical Society, Vol. 69, pp. 567 - 584, (1936)

9) Nichols, George W., "Electrolytic Manganese Dioxide", Transactions of the Electrochemical Society, Vol. 62, pp. 392 - 403, (1932)

10) Bradt, W. E., and Taylor, L. R.,
"The Electrodeposition of Manganese from Aqueous Solutions" Transactions of the Electrochemical Society, Vol. 73, pp. 327 - 337, (1938)

11) Hill, Fred J., "The Electrodeposition of Manganese from Certain Aqueous Solutions", Montana School of Mines Thesis, (1935)

12) Wallace, Wm. C., "The Electrodeposition of Manganese from Certain Aqueous Solutions", Montana School of Mines, Thesis, (1938)